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UNITED STATES DEPARTMENT OF THE INTERIOR

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TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

atm	atmosphere, standard	psig	pound (force) per square inch, gauge
°C	degree Celsius	SLM	standard liter per minute
cm	centimeter	st	short ton
g	gram	wt pct	weight percent
h	hour	yr	year
L	liter		
pct	percent		

RECOVERY OF CRITICAL METALS BY CARBONYL PROCESSING

By A. Visnapuu[1] and L. C. George[2]

ABSTRACT

The Bureau of Mines investigated carbonyl processing techniques for the recovery of the critical metals Ni, Co, Mn, and Cr from domestic primary and secondary sources. In most cases, the source materials require reductive precarbonylation treatment to metallize the contained Fe, Ni, and Co compounds to render them reactive with CO. The critical metals were recovered either by direct conversion to the respective carbonyls or as upgraded products by carbonyl removal of an undesirable metal. Best metal-to-metal carbonyl conversion was under CO pressure, from 80 atm upward, and at 140° C. Carbonylation was accelerated by the addition of H_2S in small quantities. CO pressure, temperature, promoter and pretreatment trends, and other factors enhancing metal carbonyl formation are presented.

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INTRODUCTION

The United States relies on imports for one-half to nearly all of its Ni, Co, Mn, and Cr needs. These metals are considered critical to defense requirements, either to support the Nation's industrial base or in direct military application, and are essential in maintaining a normal domestic economy. Nickel is used as an alloying addition in stainless and heat-resistant steels, in superalloys, and in other nonferrous alloys. Nickel is also used extensively in electroplating and as a catalyst in chemical processing. Cobalt metal is used primarily in heat- and corrosion-resistant alloys, in cutting and wear-resistant materials, and in magnetic alloys. Cobalt is also used in producing decolorizers, dyes, dryers, pigments and oxidizers in paints and ceramics, and catalysts for chemical processing. Manganese is essential to the production of virtually all steels and is important to the production of cast iron. It is an important constituent in Al alloys, and in the manufacture of welding-rod coatings, and is used to color bricks and ceramics. Chromium is used to prepare stainless, full-alloy, high-strength low-alloy, and electrical steels. Chromite is used to manufacture bricks to line metallurgical furnaces and is the starting material for a wide range of Cr chemicals (1-4).[3]

In 1984, the United States consumed 186,500 st Ni, 6,470 st Co, 626,800 st Mn, and 314,800 st Cr. During the same year, there was no domestic mine production of Co and Cr, and Mn was produced only in small amounts as an Fe ore coproduct. One U.S. Ni mine operated during 1984, and other domestic mine production was derived as a byproduct from domestic Cu refineries. Some of the domestic demand, ranging from 5 pct for Co to 25 pct for Ni, is derived from secondary sources or recycling. The nearly complete dependence on imports for these four critical metals makes the United States vulnerable to uncertain foreign sources or disrupted supply lines. To reduce this potentially serious loss or disruption of critical metal supply, the Bureau of Mines has conducted research to recover these metals from available or potential domestic sources (5-25). This report summarizes the results of laboratory investigations to extract Ni, Co, and Cr from domestic ores, mineral concentrates, metallurgical intermediates, mineral processing byproducts, and wastes, using carbonyl technology. Carbonyl technology was also investigated as a means to upgrade domestic Fe-containing Mn ores by extracting the Fe component as Fe carbonyl.

Metals in periodic table groups VIB, VIIB, and VIII react with CO under certain conditions to form a series of volatile carbonyl compounds that have properties potentially suitable for extractive metallurgy. The reactions take place under elevated CO pressure, from 100° to 200° C, and the compounds readily decompose under atmospheric pressure in the 100° to 300° C range. Nickel, iron, and cobalt carbonyls are the easiest to form and are produced by reaction of CO with the metals in the reduced state. The basic approach is to subject the Ni-, Fe-, or Co-containing material to solid-state reduction to metallize the metal to be extracted, treat the charge with CO to form the metal carbonyl, remove the metal carbonyl from the reactor by vapor transport and condensation, and recover the metal by thermal decomposition. This technique also is applicable to upgrading concentrates by extracting an undesirable metal component.

A number of extractive processes based on the formation of metal carbonyls have been investigated or used. High-purity Ni was produced by the Mond process for over 70 yr, and more recently the Inco pressure carbonyl process was developed to permit simultaneous extraction of Ni, Co, and Fe from mineral concentrates and metallurgical intermediates (26). Lewis (27) investigated the recovery of Ni and Fe from lateritic ores. Over 90 pct of the Ni and nearly 90 pct of the Fe was recovered in the temperature range 110°

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

to 130° C using small additions of NH_3 to the CO to improve recovery. Rhee (28) found best conversion at 121° C for reduced Fe ore flotation tailings. Dufour-Berte (29) used a fluidized-bed reactor for reduction of Fe oxide with H_2 and subsequent carbonyl formation at temperatures between 150° and 170° C and pressures between 25 and 100 atm. Okamura (30) reported the optimum temperature for carbonylation of reduced Fe oxides as 180° C at 200 atm and 130° C at 100 atm. Mond (31) reported that 200° C is optimum for $Fe(CO)_6$ formation at all pressures between 100 and 300 atm. Visnapuu (32) produced synthetic rutile from reduced ilmenite by carbonyl extraction of the excess Fe in the range of 110° to 130° C and 70 to 100 atm pressure. Visnapuu (33-35) also upgraded reduced chromite concentrates by carbonyl extraction of the excess Fe at 140° C and 100 atm CO pressure.

Common to all the carbonyl processes is the need to catalyze or promote the reaction. Sulfur or sulfur compounds have been favored for this; without the increase in reaction rate effected by them, commercial extraction of Ni and Fe as carbonyls from reduced metals probably would not be practical (26). Although the mechanism by which sulfide ions activate the metal surface and make it reactive is not precisely known, there is evidence that no more than a monolayer of the metal surface is involved. Queneau (26) reported that in amounts up to a monolayer the metal surface is composed of the metal and sulfide ions, approximating the crystal habit and stoichiometry of the most stable sulfide. He proposed that activation is the result of interference with normal bonds existing on a clean metal surface, thereby producing atoms that are nearly free. In the presence of absorbed CO, such atoms form an activated metal-CO complex, which then builds up into the metal carbonyl. The surface remains uniformly active by the continuous remaking of the sulfide-metal bonds that rupture when metal carbonyl is removed from the surface by volatilization. According to Heincke (36), a set of intermediate metal-carbonyl sulfides are formed that lower the apparent activation energy of carbonyl formation. In either case, a very small amount of S is required and excess S hinders the reaction.

EXPERIMENTAL PROCEDURE

The carbonylation tests were performed in two stainless steel high-pressure reaction vessels. Small samples weighing up to 40 g were carbonylated in a 0.55-L reaction vessel, and samples up to 250 g, or multiple samples, were tested in a 4.52-L reaction vessel. The reactors were encased in electrical heating jackets, and the temperature was measured by an Fe-constantan thermocouple in a well attached to the inside of each reactor cap. Commercial CO was supplied through a high-pressure regulator, valves, tubing, and connections in the removable cap and was discharged through a metering valve in the reactor bottom or cap. Auxiliary connections and valves were attached to the inlet tubing to admit purge gases and promoters. Exit gas flow was measured by a precision-bore rotameter downstream from the metering valve. No stirring or shaking mechanism was used.

Samples were inserted into the small reactor in fused silica, ceramic, or glass boats and into the large reactor either in similar boats or directly. The reactors were maintained at temperature between experiments, and the charges were loaded into heated reactors. Following loading, the reactors were closed and purged with the desired gas before the promoter and CO were added. Duration of the purge varied, but it was at least long enough for the reactor temperature to stabilize and a minimum of five reactor volumes of purge gas to pass through. Test duration was measured from the time the reactor attained the test pressure to the time depressurization began. A nominal 0.15- or 0.30-SLM CO flow was maintained through the reactor to vapor-transport part of the metal carbonyls from the reactor. The gases were passed at atmospheric pressure through a

3.0-cm-diam borosilicate tube maintained at 250° C in a 45-cm-long tube furnace. Low-volatility metal carbonyls of Co and Cr tended to condense on the tubing leading the reactor, wheras high-volatility carbonyls of Fe and Ni decomposed in the furnace hot zone back to CO and the respective metals, which plated out on the borosilicate tube. All CO from the process was flared as a safety precaution.

A variety of precarbonylation treatments, depending on the mineralogy of the concentrates, were required to render the concentrates reactive with CO. Specific treatments included solid-state reduction with H_2, H_2O-vapor-entrained H_2, and CO, or an air roast followed by any of the three preceding reductions. Concentrates composed of metal oxides required only a solid-state reduction, whereas concentrates that also contained metal sulfides required an oxidation roast prior to reduction to convert the metal sulfides to oxides. Oxidation roasts were conducted in the range 700° to 1,040° C for periods of from 16 to 48 h. Reductions were made in the range 600° to 1,300° C for periods of from 16 to 32 h. No evidence of concentrate melting was observed except in the few cases where the reduction temperature approached 1,300° C, although in some cases concentrate sintering was evident from approximately 900° C upward.

The reductions were performed in a large high-temperature H_2-reduction furnace or in a mullite tube heated by a small high-temperature tube furnace. All oxidation roasts were performed in the combined mullite tube and high-temperature tube furnace. Reduction and purge gas flow was 2.4 SLM through the large furnace and 0.5 SLM through the small tube furnace. In H_2 reduction, the charges were heated to 400° C under He, heated from 400° C through reduction and cooled back to 400° C under H_2, and cooled to ambient under He. In CO reduction, the charges were heated to 400° C under He, heated from 400° C through completion of reduction under CO, and cooled to ambient under He. The complete oxidation cycle of heat, hold, and cool was under flow of air. Details of the oxidation-reduction pretreatments for the specific concentrates are included in the "Results and Discussion" section. The amounts of elements O, S, Pb, and Zn extracted during the pretreatments are not included in the reported extractions.

The amount of metal extracted from the concentrates by carbonylation was calculated from charge weight loss and by chemical analysis of the residual charge. Total elemental metal in the concentrates was determined by oxidation-reduction titration or by inductively coupled plasma (ICP) emission spectrometry. Atomic absorption and gravimetric methods were used to determine accessory mineral elements such as Al, Mg, and Si. Since only Fe, Ni, and Co reacted with CO, weight loss was used as a rapid means to estimate the effectiveness of carbonyl treatment and was verified by chemical analysis of selected samples.

RESULTS AND DISCUSSION

MANGANESE ORE

Iron-containing Mn ore from Aroostook County, ME, was upgraded by carbonyl processing. The ore analyzed 9.7 pct Mn and 37.3 pct Fe with a stratified, inhomogeneous Fe distribution. First the ore was batch solid-state reduced to metallize the Fe oxide components, and then it was treated with CO to convert the metallized Fe to $Fe(CO)_5$, which was similar to the carbonyl conversion of ilmenite to synthetic rutile (32) and the upgrading of high-Fe chromite concentrates (33-35).

Table 1 presents representative processing data on Aroostook Mn ores that were batch reduced with H_2 in the 600° to 890° C temperature range and then subjected to carbonylation at 140° C under 1,500 psig CO pressure. The data indicate that a wide range of reduction temperatures can be used to prepare the ore for carbonylation. Iron extraction was better than 96 pct on samples reduced at 600°, 740°, and 790° C and slightly less on ore reduced at 890° C. Also apparent is that 2-h carbonylation reduced Fe extraction slightly, in comparison with

TABLE 1. - Dependence of Aroostook manganese ore iron extraction on solid-state reduction and carbonylation

(15-g reduction charge, 16-h H_2 reduction, 5-g carbonylation charge, 24-h carbonylation, 1,500-psig CO pressure, 0.15-SLM CO flow, 140° C, 20:1 contained Fe-H_2S promoter mol ratio, and He purge)

Reduction temp, °C	Reduction			Carbonylation			Fe extraction, pct
	Weight loss, pct	Analysis, wt pct		Weight loss, pct	Analysis, wt pct		
		Mn	Fe		Mn	Fe	
NR.....	0	9.7	37.3	4.91	10.8	35.0	10.8
600.....	18.54	13.1	45.2	42.59	19.9	3.13	96.1
720[1].....	18.80	15.3	45.9	40.32	23.4	5.63	92.7
740[2].....	19.17	13.2	45.3	26.77	16.4	26.4	58.1
740.....	19.17	13.2	45.3	43.14	22.9	2.38	97.1
790[3].....	19.45	9.3	47.4	33.10	19.2	9.50	86.3
790.....	19.45	9.3	47.4	42.83	19.6	3.25	96.0
890.....	20.03	12.2	47.8	36.67	17.2	10.4	85.9

NR Not reduced.
[1]150-g batch reduction, 250-g batch carbonylation.
[2]No H_2S promoter.
[3]2-h carbonylation.

24-h carbonylation. Iron extraction was nearly halved without addition of H_2S promoter. Over 10 pct Fe was extracted from the as-received ore by carbonylation, in agreement with petrographic observation that some of the Fe is present in the metallic state in the natural ore.

Removal of the Fe not only results in an upgraded product but also causes the material to have an increased porosity and an increased surface area of exposed Mn oxide that would facilitate dissolution. The Mn-to-Fe mol ratio in the ore increased from 0.26:1 to better than 5:1, and this would be a major factor in preventing Fe oxide solubilization and would reduce costs in subsequent leaching processes. The $Fe(CO)_5$ produced during processing was converted to Fe powder.

IRON-COBALT-NICKEL-CONTAINING MATERIALS

Copper Matte From Missouri Lead Smelters

Copper mattes from Missouri Pb smelters are a potential source of Co and Ni. The mattes initially contain less than 0.5 pct Co and Ni, but through mineral beneficiation, the Co content can be increased to 1.5 to 3 pct and the Ni content to 2 to 3 pct. In addition to the Co and Ni, the concentrates produced from these mattes also contain approximately, in percent, 20 Fe, 15 to 20 Cu, 10 to 15 Pb, and 25 to 30 S. The feasibility of carbonyl Co and Ni extraction was investigated with two such concentrates. Both were subjected to precarbonylation treatment and carbonyl processing tests, and the results are summarized in tables 2, 3, and 4.

The concentrates were subjected to either one or two roasts under the temperatures and gases indicated in table 2 and in the process lost the amount of weight shown. The objective of the precarbonylation treatments was to reduce the Fe, Co, and Ni to the metallized state to promote reactivity with the CO. The chemical analyses of the two concentrates before any precarbonylation treatment and after the various treatments are given in table 3. Combined concentrate weight-loss data and chemical analysis indicate that during the precarbonylation treatment, Pb and S were extracted from the concentrate, but Fe, Co, Ni, and Cu were not. Roasts at temperatures in excess of 1,000° C volatilized all the Pb and PbS, whereas at lower temperatures, some of the Pb remained. A single

TABLE 2. - Precarbonylation treatment of copper matte from Missouri lead smelters

Concentrate	First treatment				Second treatment			
	No. of tests	Temp, °C	Gas used[1]	Weight loss, pct	No. of tests	Temp, °C	Gas used[1]	Weight loss, pct
A1.....	3	1,250	CO....	31.48±1.32	NT	NAp	NAp...	NAp
A2.....	2	1,250	He....	28.52± .02	NT	NAp	NAp...	NAp
A3.....	1	1,150	H_2....	35.19	NT	NAp	NAp...	NAp
A4.....	2	1,270	CO....	24.75±7.20	1	1,220	H_2+H_2O	33.32
A5.....	4	1,150	H_2....	35.71±2.49	4	1,220	H_2+H_2O	8.39±3.93
B1.....	3	1,220	H_2....	45.52±2.44	NT	NAp	NAp...	NAp
B2.....	1	920	H_2+H_2O	36.51	NT	NAp	NAp...	NAp
B3.....	7	1,220	H_2+H_2O	41.66±1.44	NT	NAp	NAp...	NAp
B4.....	3	820	Air...	18.35± .17	3	920	H_2+H_2O	34.13±3.07
B5.....	1	820	Air...	18.08	1	1,040	H_2+H_2O	35.55
B6.....	1	920	Air...	26.38	1	920	H_2+H_2O	28.52
B7.....	3	920	Air...	22.39± .46	3	1,040	H_2+H_2O	33.38± .07
B8.....	1	930	Air...	19.54	1	930	H_2+H_2O	14.21
B9.....	1	940	Air...	31.16	1	940	H_2....	28.11
B10.....	1	940	Air...	29.58	1	1,210	H_2....	32.87

NAp Not applicable. NT Not treated. [1]H_2+H_2O means H_2O-entrained H_2.

TABLE 3. - Analysis of copper matte concentrates from Missouri lead smelters before and after precarbonylation treatments

Concentrate	No. of tests	Analysis, wt pct					
		Fe	Co	Ni	Cu	Pb	S
A (untreated)	7	21.2±1.4	1.79±0.14	2.56±0.20	21.5±2.3	9.94±0.76	30.8 ±0.7
A1.....	3	26.4±3.6	2.41± .79	3.18± .95	27.1± .4	.04± .02	23.4 ±1.2
A2.....	1	29.6	2.56	3.88	30.2	.02	26.4
A3.....	1	33.0	2.60	4.10	40.0	.01	17.0
A4.....	1	47.4	3.08	4.93	40.6	ND	ND
A5.....	4	38.4±5.9	3.39± .52	4.52± .61	34.3±3.5	ND	9.83± .64
B (untreated)	3	21.8± .1	2.18± .15	2.93± .25	15.1± .9	10.1 ± .9	25.8 ± .2
B1.....	3	35.5±2.2	3.56± .31	4.66± .47	23.8± .4	.07± .07	13.5 ±1.5
B2.....	1	30.7	3.58	4.42	ND	6.00	19.2
B3.....	8	35.6±1.5	3.96± .28	5.05± .18	23.6±1.6	.04± .02	13.3 ±2.7
B4.....	3	39.1±2.1	4.29± .22	5.88± .11	27.4± .3	3.22±4.49	.60± .14
B5.....	1	43.1	4.31	6.04	28.8	.28	.09
B6.....	2	39.3± .6	4.20± .04	5.30± .18	26.2± .1	6.00± .12	.11± .03
B7.....	4	40.6±2.4	4.20± .29	5.63± .21	28.1±1.6	.42± .23	.02± .01
B8.....	1	30.3	3.60	4.20	20.4	19.6	.08
B9.....	1	38.5	4.05	5.52	ND	4.52	.02
B10.....	1	39.6	4.00	5.60	ND	.06	.38

ND Not determined.

solid-state reductive roast, irrespective of the temperature, did not extract all of S; however, an air roast to convert the metal sulfides to oxides, followed by solid-state reduction, resulted in nearly complete removal of the S.

Table 4 summarizes the carbonyl-extraction test results for the two concentrates. Data in column 3 of the table give mol ratio of combined Fe, Co, and Ni to H_2S promoter at the start of each test; "None" indicates that no H_2S was added. Extraction percentages are based on the average chemical analyses of precarbonylation-treated concentrate and carbonyl-treated concentrate and the weight loss during carbonylation. The Fe, Co, and Ni extraction values result

TABLE 4. - Metal extraction from copper matte from Missouri lead smelters by carbonylation

(1- to 10-g charge, 1,500-psig CO pressure, 0.15-SLM CO flow, 140° C, and He purge)

Concentrate	No. of tests	(Fe+Co+Ni) -H_2S mol ratio	Time, h	Weight loss, pct	Analysis, wt pct						Extraction, pct					
					Fe	Co	Ni	Cu	Pb	S	Fe	Co	Ni	Cu	Pb	S
A1.....	3	29.4:1	24	7.39± 0.42	24.8 ±2.7	2.63±0.29	1.49±0.47	30.8± 4.6	0.01±0	ND	13.0	-1.1	56.6	-5.3	76.8	ND
A2.....	1	None	24	4.56	28.8	2.69	1.93	33.2	.05	27.1	7.1	- .3	52.5	-4.9	-139	2.0
	1	33.1:1	24	8.29	24.4	2.64	.93	30.9	.05	29.4	24.4	5.4	78.0	2.3	-129	-2.1
A3.....	1	None	72	2.95	33.9	5.60	3.26	33.8	.03	19.4	.3	-109	30.4	4.2	-191	-10.8
	3	36.5:1	24	6.92± 1.09	31.4 ±1.6	3.02± .16	2.94± .15	39.5± .8	.03± .03	19.4 ±0.9	11.4	-8.1	33.3	8.1	-179	-6.2
	2	36.5:1	48	7.47± 2.22	31.2 ±1.5	3.20±0	3.10± .42	40.0± .1	.02± .02	20.0 ± .3	12.5	-13.9	30.0	7.5	-85.1	-8.9
	1	9.1:1	24	19.84	23.0	4.15	1.14	44.7	.01	24.4	44.1	-27.9	77.7	10.4	19.8	-15.1
	3	9.1:1	72	21.90± 2.28	19.7 ±1.7	4.94±1.29	1 ± .39	43.8± 4.2	.34± .28	23.7 ±1.2	53.4	-48.4	81.0	14.5	-2,555	-8.9
	2	4.6:1	72	24.36± 2.13	18.0 ±2.3	5.23±1.34	.40± .16	ND	.02± .01	25.2 ± .1	58.7	-52.4	92.6	ND	-51.3	-12.1
A4.....	1	12.9:1	24	42.52	9.34	3.68	1.66	70.5	ND	5.9	88.7	42.5	80.6	.2	ND	ND
A5.....	2	None	72	11.42± .08	30.6 ±6.4	3.74± .73	3.58± .82	33.2± 8.6	ND	11.1 ±2.5	29.4	2.3	29.8	14.3	ND	0
	2	46.6:1	24	7.35± .01	38.5 ±0	3.76± .13	4.22± .08	40.4± 1.5	.01± .01	9.25±2.47	7.1	-2.8	13.5	-9.1	ND	12.8
	2	21.3:1	24	17.84± .40	23.8 ±5.7	3.42± .64	2.45± .27	37.0±10.0	ND	10.3 ±0	49.1	17.1	55.5	11.4	ND	13.9
	6	10.6:1	24	29.10± 3.24	15.9 ±4.5	4.58±1.80	1.95± .54	44.2±12.2	.02± .02	15.6 ±1.3	70.6	4.2	69.4	8.6	ND	-12.5
	1	10.6:1	72	40.58	5.02	5.54	.38	62.8	.03	18.4	92.2	2.9	95.0	-8.8	ND	-11.2
	2	5.3:1	24	31.87± .85	10.2 ±5.0	3.76±1.08	.62± .55	55.5± 1.4	.01±0	18.6	80.7	24.4	91.7	-10.2	ND	-28.9
	1	5.3:1	72	35.22	5.15	6.54	.15	ND	.05	21.8	91.3	-25.0	97.9	ND	ND	-43.7
B1.....	1	None	72	4.40	31.3	7.98	3.78	23.5	.06	.15	15.7	-114	22.5	5.6	18.1	98.9
	2	43.9:1	24	7.54± .43	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	2	10.0:1	24	20.67± 1.40	20.7 ± .6	4.71± .40	1.24± .06	28.8± .8	.04±0	19.2 ± .8	53.7	-5.0	78.9	4.0	54.7	-12.8
	4	10.0:1	72	22.00± 5.56	17.2 ±2.2	5.98± .72	.64± .48	30.0± 1.9	.31± .49	21.2 ± .7	62.2	-31.0	89.2	1.7	-245	-22.5
	2	5.0:1	24	21.27± 1.60	18.4 ± .7	4.64± .27	.50± .07	29.4± .7	.02± .01	21.4 ± .3	59.2	-2.6	91.6	2.7	77.5	-24.8
B2.....	2	8.9:1	72	5.72± .91	22.4 ±2.8	3.40± .45	.84± .01	19.5	5.74± .86	22.7 ± .6	31.2	10.5	82.1	ND	9.8	-11.5
	1	4.4:1	72	6.18	22.7	3.06	.04	ND	5.37	23.7	30.6	19.8	86.4	ND	16.0	-15.8
B3.....	2	None	72	5.06± .08	33.0 ±1.8	6.15±0.30	3.23± .21	26.4± 0.6	.05±0	13.4 ±2.5	12.0	-47.4	39.3	-6.2	-18.7	4.3
	4	10.2:1	24	28.89± 1.52	13.4 ± .8	5.01± .34	.63± .16	34.3± 2.2	.01±0	18.6 ± .7	73.2	10.0	91.1	-3.4	82.2	.6
	8	10.2:1	72	23.73± 6.64	17.0 ±3.6	5.86±1.27	.74± .48	33.1± 4.6	.09± .11	19.4 ±2.3	63.6	-12.9	88.8	-7.0	-71.6	-11.3
	2	5.1:1	24	28.20± 1.30	13.0 ± .1	5.02± .44	.14± .04	34.1± 1.1	.01±0	21.0 ± .1	73.8	9.0	98.0	-3.7	82.0	-13.4
	6	5.1:1	72	23.90± 2.67	17.1 ±2.4	4.87±1.34	.33± .17	ND	.02± .03	22.2 ± .1	63.4	6.4	95.0	ND	62.0	-27.0
B4.....	2	None	72	22.44± .81	24.6 ± .6	3.48± .19	2.76± .80	34.8± 2.1	10.4 ± .2	.58± .04	51.2	37.1	63.6	1.5	-4.0	25.0
	4	11.3:1	24	25.81± 4.38	21.6 ±2.6	3.53± .25	3.39± .79	37.8± 3.0	3.42±4.61	2.90± .30	59.0	39.0	57.2	-2.3	21.2	-259
	7	11.3:1	72	35.09± 5.88	10.2 ±5.4	2.34± .75	1.70± .60	40.2± 3.7	8.79±5.37	4.20± .94	83.1	64.6	81.2	-8.8	-102	-354
	4	5.6:1	72	37.97±11.11	8.94±1.81	3.10±1.01	1.38± .21	ND	11.5±.3	7.28± .60	85.8	55.2	85.4	ND	-122	-653
B5.....	1	None	72	21.92	29.3	3.43	4.52	35.4	.35	ND	46.9	37.9	41.6	4.0	2.4	ND
	6	12.3:1	24	18.72± 4.30	28.4 ±4.7	4.28± .42	4.72± .58	34.7± 2.6	.37± .05	2.12±1.28	46.4	19.3	36.5	2.1	-7.4	-1,815
	1	12.3:1	72	39.77	10.5	1.98	1.52	44.8	.37	3.66	85.3	72.3	84.8	6.3	20.4	-2,349
B6.....	7	11.3:1	72	34.69± 4.31	14.0 ±5.6	2.52± .45	2.16± .66	36.9± 3.0	7.09±1.96	3.57±2.19	76.7	60.8	73.4	8.0	22.8	-2,020
	2	5.6:1	72	34.42± 3.17	10.2 ±3.4	3.33±1.20	1.62± .06	41.9± 1.1	8.30±0	5.59±1.17	83.0	48.0	80.0	-4.9	9.3	-3,233
B7.....	2	None	72	24.02± 1.07	28.7 ±1.4	3.32± .01	4.34± .18	36.7± 1.0	.77± .01	.12± .13	46.3	39.9	41.4	.8	-39.3	- 356
	2	11.6:1	24	21.56± .85	27.9 ±1.8	4.16± .13	3.86± .32	35.6± 1.1	.28± .05	2.10±0	46.1	22.3	46.2	.6	47.7	-8,136
	7	11.6:1	72	37.75± 2.80	12.1 ±2.3	2.79± .56	1.97± .32	44.3± 4.0	.70± .45	2.86± .86	81.4	58.6	78.2	1.9	-3.8	-8,801
	4	5.8:1	72	36.10± 2.67	9.69± .53	4.41± .88	1.47± .15	37.9± 9.8	1.03± .06	6.00±1.06	84.7	32.9	83.3	13.8	-56.7	-19,070
B8.....	3	8.7:1	72	28.84± 3.05	6.13±3.82	1.29± .78	.92± .49	27.0± 4.9	25.0 ±4.0	2.22± .23	85.6	74.5	84.4	5.8	9.2	-1,875
	2	4.4:1	72	26.51± 3.48	6.46±1.53	1.79± .51	.97± .18	28.8± 1.4	21.8 ±9.1	5.26± .81	84.3	63.5	83.0	-3.8	18.3	-4,732
B9.....	5	11.0:1	72	41.54± 2.30	6.91±2.33	3.28±1.01	1.31± .53	36.7	7.43± .49	4.38±1.48	89.5	52.7	86.1	ND	3.9	-12,702
B10.....	1	11.3:1	72	28.08	22.7	4.46	3.05	34.5	.33	5.85	58.8	19.8	60.8	ND	-296	-1,007
	1	11.3:1	72	8.93	37.5	5.00	5.90	ND	ND	2.10	13.8	-13.8	4.1	ND	ND	- 403

ND Not determined

from carbonyl processing, whereas no significant S and no Cu and Pb extraction is expected during this step. Negative values in the extraction columns indicate that the concentration of certain elements was greater in the product than in the starting concentrate as a result of weight loss during carbonyl processing. For Cu, this is attributed to experimental variance in analytical results of the starting and product concentrates as indicated by persistent values around the expected zero extraction. Similarly, Pb extraction during carbonylation should be zero, but since the levels were extremely low in the starting and product concentrates, small variances in chemical analysis for the respective total concentrations may have led to large, spurious extraction percent values.

Sulfur extraction values are susceptible to two influences: (1) The CO may react with the contained S to form COS and extract some of the S; (2) S from the H_2S promoter reacts with the clean metal surface to form a stable sulfide on the surface, which activates the carbonyl reaction. The results indicate that the latter was the case because of the large and persistent increase in the S level following carbonylation tests where H_2S was used as the promoter, especially in concentrates where most of the S had been removed prior to carbonylation tests.

Concentrate A was not treated with a precarbonylation air roast, whereas an air roast was the first precarbonylation treatment for concentrates designated B4 through B10. It is evident that the calculated Co extraction percentage correlates well with air-roasted concentrates. Variance in Co extraction is great for non-air-roasted concentrates, with results ranging from an indicated Co gain in the product to around 40 pct extraction; however, for concentrates with an air roast followed by solid-state H_2 reduction, the calculated Co extraction is higher and much more consistent. The increased extraction appears to be due to the absence of S in the concentrate subjected to carbonylation. No significant improvement in Fe and Ni extraction was realized when the concentrate was air-roasted prior to solid-state reduction compared to solid-state only reduction, since over 90 pct of both metals was extracted with the two approaches. Carbonylation over extended time spans improved metal extraction even though 72 h did not result in better than 75 pct Co removal. Hydrogen sulfide again improved metal-to-carbonyl conversion, and the best combined metal-H_2S ratio appears to be (9-12):1 from data in table 4.

Carbothermic-Reduced Lead Blast Furnace Slag

Another material subjected to carbonyl processing to extract Co values was carbothermic-reduced Pb blast furnace slag, characterized in tables 5 and 6. Iron was the major constituent, accounting for over 75 pct of the composition. Sulfur accounted for over 11 pct, Cu for 1.6, and the carbonyl-forming Co and Ni for 1.08 and 0.16 pct, respectively. The material was also subjected to a number of precarbonylation treatments, as summarized in table 5. Only part of the S was extracted during the solid-state reduction, and air or He roast followed by solid-state reduction was necessary for complete S removal. Sulfur removal also improved with an increase in treatment temperature. Lead and zinc volatilized from the charge, and Fe, Co, Ni, and Cu were concentrated during the precarbonylation processing.

Table 7 summarizes the carbonyl extraction test results for the carbothermic-reduced Pb blast furnace slag. Because most of the Fe and Ni were initially in a metallized condition, excellent Fe and Ni carbonylation was achieved without pretreatment. Iron and nickel extraction remained excellent when the material was subjected to the reduction or oxidation pretreatment followed by reductive precarbonylation treatments, whereas, Co extraction approached good levels most often when the precarbonylation treatment removed maximum S and H_2S promoter addition was minimal. Extended carbonylation time also improved Co extraction and to a lesser extent, Fe and Ni extraction. Sulfur extraction percentages in table 7 indicate an increase in S content, which is attributed to retention of S on the

TABLE 5. - Precarbonylation treatment of carbothermic-reduced lead blast furnace slag

Concentrate	First treatment				Second treatment			
	No. of tests	Temp, °C	Gas used[1]	Weight loss, pct	No. of tests	Temp, °C	Gas used[1]	Weight loss, pct
C1.....	1	1,240	CO....	8.17	NT	NAp	NAp...	NAp
C2.....	2	1,250	He....	.56±0.08	NT	NAp	NAp...	NAp
C3.....	2	720	H_2+H_2O	3.38± .11	NT	NAp	NAp...	NAp
C4.....	2	1,220	H_2+H_2O	8.62± .12	NT	NAp	NAp...	NAp
C5.....	2	1,250	He....	.56± .08	1	1,220	H_2+H_2O	14.95
C6.....	2	700	Air...	-21.39± .14	2	830	H_2....	29.02±1.43
C7.....	2	825	Air...	-21.61±1.69	3	830	H_2....	26.27±4.41
C8.....	1	930	Air...	-20.61	1	940	H_2....	29.44
C9.....	1	1,040	Air...	-18.26	2	840	H_2....	28.78± .01
C10.....	1	930	Air...	-22.18	1	930	H_2+H_2O	30.30

NAp Not applicable. NT Not treated. [1]H_2+H_2O means H_2O-entrained H_2.

TABLE 6. - Analysis of carbothermic-reduced lead blast furnace slag before and after precarbonylation treatments

Concentrate	No. of tests	Analysis, wt pct							
		Fe	Co	Ni	Cu	Pb	S	O	Zn
C (untreated).....	2	76.6±3.4	1.08±0.02	0.16±0	1.60±0.10	0.30±0	11.03±1.8	ND	0.40±0
C1.....	NAp	ND	ND	ND	ND	ND	ND	ND	ND
C2.....	NAp	ND	ND	ND	ND	ND	ND	ND	ND
C3.....	2	85.9± .1	1.45± .07	.16±0	ND	ND	8.28± .04	ND	ND
C4.....	2	89.5±1.6	1.45± .08	.19± .03	1.73±0	ND	6.24± .21	ND	ND
C5.....	1	90.2	1.68	.23	2.25	ND	.16	ND	ND
C6.....	2	91.3±2.0	1.52±0	.18± .01	1.92± .06	ND	1.38±1.59	ND	ND
C7.....	3	87.9±7.3	1.60±0	.19± .02	2.07± .31	.05±0	4.89±5.23	ND	ND
C8.....	2	88.4±5.7	1.46± .51	.18± .02	2.32	.01	.06± .01	2.02±2.01	.02
C9.....	2	90.2± .2	1.50±0	.21±0	2.20±0	.05±0	.02±0	ND	.01±0
C10.....	2	91.8±7.6	1.68± .12	.22± .04	2.22	.01	.82± .13	3.97±4.77	.02

NAp Not applicable. ND Not determined.

TABLE 7. - Metal extraction from carbothermic-reduced lead blast furnace slag by carbonylation

(1- to 10-g charge, 1,500-psig CO pressure, 0.15-SLM CO flow, 140° C, and He purge)

Concentrate	No. of tests	(Fe+Co+Ni) -H_2S mol ratio	Time, h	Weight loss, pct	Analysis, wt pct							Extraction, pct						
					Fe	Co	Ni	Cu	Pb	S	O	Fe	Co	Ni	Cu	Pb	S	O
C (untreated)	1	None	24	44.90	64.2	2.35	0.07	3.11	0.56	22.6	ND	53.8	-19.9	75.9	-7.1	-2.9	-10.2	ND
	1	72.1:1	2	15.33	63.8	.82	.12	1.32	ND	15.1	ND	29.5	35.7	36.5	30.1	ND	-13.1	ND
	[1]1	66.9:1	24	37.80	47.3	1.32	.09	2.13	ND	20.7	ND	61.6	24.0	65.0	17.2	ND	-13.9	ND
	3	72.1:1	24	52.01±2.52	43.1±15.5	1.85±0.39	.06±0.03	2.60± 0.59	.61	27.3 ± 1.4	ND	67.4	17.8	82.0	22.0	2.5	-15.9	ND
	[1]1	66.8:1	48	49.11	59.0	2.20	.05	3.50	.62	25.5	ND	60.8	-3.7	84.1	-11.3	-5.2	-14.8	ND
	1	72.1:1	48	57.56	51.9	3.00	.01	4.20	.73	30.5	ND	71.2	-17.9	97.3	-11.4	-3.3	-14.6	ND
	2	18.0:1	24	53.52±1.25	49.8± 2.8	2.19± .22	.02± .01	3.27± .57	.70±0.06	30.2 ± 1.1	ND	69.8	5.7	94.3	5.0	-8.5	-24.2	ND
C1	1	78.5:1	24	24.55	16.7	.39	.13	.56	ND	11.6	ND	84.9	75.0	43.7	75.8	ND	28.9	ND
C2	1	72.5:1	24	32.98	12.3	2.20	.18	2.40	.01	17.9	ND	45.8	-35.8	25.0	0	97.8	-5.6	ND
	1	18.1:1	24	46.43	30.0	1.53	.05	1.73	.02	25.2	ND	79.1	24.5	83.4	42.4	96.4	-18.8	ND
C3	2	None	24	51.35± .96	62.2± 3.0	2.66± .06	.08± .01	ND	ND	22.1 ± .6	ND	64.8	10.8	75.7	ND	ND	-29.9	ND
	2	None	72	63.13± .30	48.8± 4.4	1.82± .36	.04± .02	4.42± .50	ND	30.5 ± 1.4	ND	79.1	53.7	90.8	ND	ND	-35.8	ND
	2	20.3:1	24	61.40± .05	49.8±0	3.08± .06	.03±0	ND	ND	32.7 ±0	ND	77.6	18.0	92.8	ND	ND	-52.4	ND
C4	[1]2	None	72	49.62± .14	72.6± 6.2	3.12± .18	.11± .01	3.80± .46	ND	12.2 ± .6	ND	59.1	-8.4	70.8	-10.7	ND	1.5	ND
	4	None	72	76.37±2.59	37.5± 6.8	8.44±1.83	.17± .10	6.71± 1.48	ND	24.4 ± 1.6	ND	90.1	-37.5	78.9	8.3	ND	7.6	ND
	[1]2	19.6:1	24	58.16± .47	72.6± 4.5	3.02± .12	.22±0	3.55± .38	ND	14.0 ± .4	ND	66.1	12.6	51.6	14.1	ND	6.1	ND
	2	21.1:1	24	75.23± .68	43.9± 1.1	6.64± .05	.12± .13	6.80± .26	ND	29.3 ± .1	ND	87.9	-13.4	84.4	2.6	ND	-16.3	ND
C5	2	None	72	86.78±5.70	31.9±31.5	3.44±1.19	.12± .01	15.3 ± 5.8	.02± .02	2.28± 2.58	ND	95.3	72.9	93.1	10.1	ND	-88.4	ND
	1	21.3:1	24	83.27	38.8	8.47	.12	12.2	.06	7.00	ND	92.8	15.7	91.3	9.3	ND	-632	ND
C6	3	None	72	91.83±3.55	11.9± 6.6	8.15±5.44	.18± .23	26.7 ±10.2	.21	ND	ND	98.9	56.2	91.8	-13.6	ND	ND	ND
	2	21.5:1	24	78.02± .95	58.2±13.2	8.08±6.25	.12± .04	7.51± 1.85	ND	7.75± 6.86	ND	86.0	-16.8	85.3	14.0	ND	-23.4	ND
	1	10.8:1	24	80.64	29.5	7.10	.02	8.53	.05	ND	ND	93.7	9.6	97.8	14.0	ND	ND	ND
C7	3	None	72	71.12±13.82	32.9±10.3	11.7 ±6.3	.06± .05	8.22± 3.28	.07	31.4	ND	89.2	-111.2	90.9	-15.8	59.6	-102	ND
	3	20.7:1	24	75.97±11.95	37.1± 6.9	6.03±2.66	.06± .02	9.15± 4.89	.08± .06	21.6 ±11.5	ND	89.9	9.4	92.4	-7.3	61.6	-15.9	ND
	1	10.4:1	24	77.63	37.1	5.80	.02	7.66	.05	ND	ND	90.6	18.9	97.6	16.4	77.6	ND	ND
C8	3	None	72	93.24± .45	15.3± 5.6	3.03±1.72	.09± .03	29.4 ± 2.5	ND	1.24± .39	22.0±1.3	98.8	86.0	96.6	14.3	ND	-39.7	26.4
	1	83.4:1	72	93.04	9.1	6.40	.05	26.7	ND	5.40	42.1	99.3	69.5	98.1	19.9	ND	-52.6	-45.1
	2	20.8:1	72	89.22± .50	14.0± 2.1	9.78±1.15	.07± .01	14.8 ± 2.5	ND	ND	ND	98.3	27.8	95.8	31.2	ND	ND	ND
C9	1	None	72	81.71	46.2	1.68	.16	9.26	ND	.30	ND	90.6	79.5	86.1	23.0	ND	-174	ND
	1	21.3:1	2	50.17	74.9	3.00	.17	4.50	.05	2.50	ND	58.6	.3	59.7	-1.9	50.2	-6,129	-49.5
	2	21.3:1	24	86.66± .11	11.1± 1.0	13.2 ±1.0	.08± .01	15.6 ± .6	.07±0	8.30± .60	ND	98.4	-17.4	94.9	5.4	81.3	-5,436	-6.7
C10	3	None	72	91.74± 2.20	23.7±15.6	4.03±2.68	.09± .06	14.9 ± 9.2	ND	4.08± 4.00	16.6±3.7	97.9	80.2	96.6	44.6	ND	58.9	65.5
	1	86.8:1	72	81.96	67.2	6.10	.14	10.8	ND	4.60	19.3	86.8	34.5	88.5	12.2	ND	-1.2	12.3
	2	21.7:1	72	89.92± 1.41	16.0± 7.8	11.4 ±1.3	.10± .03	18.2 ± 1.0	ND	ND	ND	98.2	31.6	95.4	17.4	ND	ND	ND

ND Not determined.

[1]Carbonylated at 110° C.

charge from the reaction between the H_2S promoter and the metal surface.

IRON-CHROMIUM-NICKEL-CONTAINING MATERIALS

Stainless Steel

Three stainless steel (SS) powders, 316, 410L, and 430, were tested for their response to carbonylation. The 316 austenitic and 430 Cr stainless steels were selected because of their widespread use, and the 410L hardenable Cr stainless steel was chosen because the high-pressure reactors used in these studies were made of this alloy. The 316 and 410L powders were minus 100 mesh, and the 430 powder was minus 325 mesh. Virgin powders were used instead of stainless steel scrap because of their ready availability and known composition.

Results of the carbonyl processing research on the stainless steels are summarized in table 8. Chemical analyses were performed only on samples that exhibited significant weight loss during carbonylation. The data indicate that the carbonylation response of the stainless steels is controlled by the type of reductive pretreatment, alloy composition, and promoter. Powders carbonylated as received without the H_2S promoter showed little carbonyl conversion, whereas with promoter, carbonyl conversion became apparent, especially for the Cr stainless steels. Solid-state H_2 reduction prior to carbonylation is deleterious, as there is little apparent carbonyl conversion with or without the H_2S promoter. The response of solid-state-reduced 316 SS greatly improved when the reduction was accomplished with H_2O-entrained H_2 and H_2S promoter was used during carbonyl processing. The same H_2O-entrained H_2 solid-state reduction of the 430 SS had no effect on subsequent carbonylation. The significant increase in carbonyl conversion attributable to the H_2S is in line with results on other systems.

The added significant increase in carbonyl formation for the 316 SS, resulting from the H_2O-entrained H_2 reduction, but not for similarly reduced 430 SS or H_2-reduced 316 SS, was surprising. Both stainless steels gained slightly in weight during the H_2 reduction and considerbly more during H_2O-entrained H_2 reduction. The weight gain is attributed to formation of Cr_2O_3 from the reaction of Cr with H_2O because of favorable thermodynamics (37). Segregation of some Cr in the alloy as Cr_2O_3 should enhance the reactivity of CO with the remaining Fe

TABLE 8. Metal extraction from stainless steel by carbonylation

(1- to 10-g charge, 24-h carbonylation, 1,500-psig CO pressure, 0.15-SLM CO flow, 140° C, 20:1 contained (Fe+Cr+Ni)-H_2S promoter mol ratio, and He purge)

Stainless steel	Reduction			Carbonylation				Metal extraction, pct		
	Temp, °C	Reducing gas	Weight loss, pct	Weight loss, pct	Analysis, wt pct					
					Fe	Cr	Ni	Fe	Cr	Ni
316.....	NR	NAp.....	NAp	0.78	ND	ND	ND	ND	ND	ND
	NR	NAp.....	NAp	[1].20	ND	ND	ND	ND	ND	ND
	715	H_2.....	-0.12	0	ND	ND	ND	ND	ND	ND
	715	H_2.....	-.12	[1]-.06	ND	ND	ND	ND	ND	ND
	730	H_2+H_2O..	-2.36	31.69	51.8	21.2	6.78	46.7	12.8	60.5
	730	H_2+H_2O..	-2.36	[1]3.80	63.3	17.6	8.73	8.3	-1.9	28.4
410L.....	NR	NAp.....	NAp	4.75	86.3	12.6	.10	5.2	2.0	52.4
430.....	NR	NAp.....	NAp	4.35	ND	ND	ND	ND	ND	ND
	NR	NAp.....	NAp	[1].29	ND	ND	ND	ND	ND	ND
	715	H_2.....	-.27	.05	ND	ND	ND	ND	ND	ND
	715	H_2.....	-.27	[1].10	ND	ND	ND	ND	ND	ND
	730	H_2+H_2O..	-1.29	4.65	81.8	16.2	.20	3.5	6.3	49.2
	730	H_2+H_2O..	-1.29	[1].32	ND	ND	ND	ND	ND	ND

NAp Not applicable. ND Not determined. NR Not reduced. [1]No H_2S promoter.

and Ni, since previous research has shown that Fe and Cr alloying by intermetallic diffusion in reduced chromite concentrates inhibits Fe carbonyl formation (35). The fact that carbonyl formation was enhanced in 316 SS and not in 430 SS is attributed to the greater presence of the more reactive Ni in the former. Data in table 8 show consistently greater Ni and Fe extraction and doubtful Cr extraction. The limited carbonylation tests on the three stainless steel powders indicate that, while recovery of Cr and Ni from stainless steels may not be practical, service use of stainless steels in environments containing H_2, H_2O, H_2S, and CO should be carfully evaluated.

Stainless Steel Slag

Carbonyl processing techniques were tested on a stainless steel slag that analyzed, in percent, 11.8 Cr, 1.3 Ni, 3.7 Fe, 0.07 S, and 11.1 Si, as a means to extract the Cr and Ni values. Carbonylation was performed on the slag as received and after H_2, CO, or H_2O-entrained H_2 reduction. Results of these tests are summarized in table 9.

The data in table 9 indicate no significant Cr extraction from the slag powder and erratic Ni and Fe extraction, with a higher percentage of Ni than Fe extracted in nearly all cases. Percent metal extraction values were calculated from chemical analyses of the samples, and the negative values indicate an increase of the metal after processing. This is attributed to experimental and analytical error. Precarbonylation reduction does not appear to have significant influence on carbonyl conversion, wheras grinding to minus 200 mesh to increase particle surface area after reduction improved Ni and Fe extraction. The inability to convert the Cr to the carbonyl is similar to what was observed with solid-state-reduced chromite concentrates, namely, a decrease in Fe-to-Fe $(CO)_5$ conversion due to Cr-Fe alloy formation by intermetallic diffusion as the precarbonylation reduction temperature was increased to reduce the chromium oxide fraction (35). In the stainless steel slag, the metals are already present primarily as alloys, and any of their oxides metallized during reduction would tend to alloy by intermetallic diffusion. The inability to form Cr carbonyl and the erratic and incomplete conversion of the small quantities of Ni and Fe present to the respective carbonyls tend to make the carbonyl processing approach impractical.

TABLE 9. - Metal extraction from stainless steel slag by carbonylation

(10-g charge, 24-h carbonylation, 1,500-psig CO pressure, 0.15-SLM CO flow, 140° C, 17:1 contained (Cr+Ni+Fe)-H_2S promoter mol ratio, and He purge)

Reduction			Carbonylation				Metal extraction, pct		
Temp, °C	Reducing gas	Weight loss, pct	Weight loss, pct	Analysis, wt pct					
				Cr	Ni	Fe	Cr	Ni	Fe
NR.....	NAp.....	NAp	[1]0.55	12.6	0.56	2.80	-1.1	47.5	26.6
1,200.....	H_2.....	0.77	1.67	13.2	.82	3.58	-3.9	24.5	8.1
1,200.....	H_2.....	.73	2.00	11.0	.37	2.60	13.7	66.0	33.4
1,200.....	H_2.....	.77	[2]3.31	11.6	.10	1.17	10.2	90.6	70.4
1,200.....	H_2.....	.73	[2]3.00	10.9	.16	2.41	15.4	85.5	38.9
1,300.....	CO.....	5.52	[2]4.57	14.2	.11	1.55	-3.2	90.7	63.2
1,200.....	H_2+H_2O..	1.06	3.00	9.60	.66	2.09	25.7	40.3	47.2
1,200.....	H_2+H_2O..	1.90	2.81	11.6	.63	3.17	10.8	43.3	20.5
1,200.....	H_2+H_2O..	1.90	[3].94	12.8	.81	4.5	-.3	25.8	-15.1

NAp Not applicable. NR Not reduced.

[1]6-h carbonylation under 1,200-psig CO and 4.25:1 contained (Cr+Ni+Fe)-H_2S promoter mol ratio.

[2]Minus 200 mesh.

[3]No H_2 promoter.

OTHER MATERIALS

Superalloy Scrap and Grinding Waste

Carbonyl recovery of Ni, Co, and Cr from Ni- and Co-base superalloy scrap was investigated. Carbonylation tests were performed on powder scrap samples of two Ni-base alloys, one Co-base alloy, and mixed alloy scrap analyzing over 50 pct Ni and nearly 20 pct Fe, prepared by Zn dissolution and Zn distillation at the Bureau's Reno Research Center. Also tested was automotive valve hardfacing grinding waste containing substantial Fe, Ni, Co, and Cr that was degreased by the Bureau's Salt Lake City Research Center. Chemical analyses of the five scrap samples are given in table 10.

Carbonylation tests were performed on the materials as received, after solid-state H_2 reduction, and after solid-state H_2O-entrained H_2 reduction. Representative results are summarized in table 11. For the Ni-base alloys containing minimal Fe, carbonylation weight-loss data indicate (1) the need for H_2S promoter, (2) somewhat better carbonyl conversion for the scrap as received compared with H_2 solid-state-reduced scrap, and (3) best carbonyl conversion after H_2O-entrained H_2 reduction. A consistent increase in charge weight during reduction was observed only when concentrates containing substantial Cr were reduced with H_2O-entrained H_2. The H_2O-entrained H_2 reduction resulted in weight gain, which is attributed to Cr_2O_3 formation with the consequent liberation of other alloy constituents for enhanced carbonyl formation. Metal extraction results based on chemical analysis indicate that primarily Ni was removed from the superalloy scrap.

TABLE 10. - Composition of superalloy scrap and grinding waste, weight percent

	Fe	Ni	Co	Cr	C
Superalloy:					
Ni-base 1...	0.17	58.8	8.5	16.0	0.17
Ni-base 2...	.24	61.2	10.0	8.0	.1
Co-base.....	.40	10.0	55.5	21.5	.6
Mixed.....	19.0	54.0	.41	13.0	.3
Grinding waste	27.3	11.1	14.2	18.9	2.0

Carbonylation weight-loss data for the Co-base superalloy scrap indicated best carbonyl conversion for the as-received material carbonylated at 110° C under 1,900 psig CO, although the overall conversion did not exceed 10 pct. Chemical analysis indicate that Ni, Co, and Cr were extracted in approximately equal quantities. For the mixed superalloy scrap, weight loss during carbonylation ranged from nearly 24 to almost 37 pct, with increased weight loss as the material was solid-state-reduced with H_2 and with H_2O-entrained H_2. Chemical analysis indicated that primarily Fe and Ni were converted to the respective carbonyls. The indicated increase in Co content is attributed to sample inhomogeneity and analysis variation due to the small concentration of Co in the sample.

Carbonylation of the grinding waste resulted in best case weight losses comparable to those for the superalloy scrap. One difference between it and the superalloy scrap is that it did not respond well in the as-received condition. This is reasonable since the waste particles would be expected to acquire an oxide coat during the grinding process. Solid-state H_2 or H_2O-entrained H_2 reduction rendered the material reactive with CO, and weight losses approached 20 pct. Analyses indicate that primarily Fe and Ni were extracted.

The carbonyl processing tests on the superalloy scrap and grinding waste indicate that Fe, Ni, Co, and Cr can be extracted, but the carbonyl reaction rates are considerable slower than for materials where the carbonyl-susceptible components are in an elemental-reduced, metallic state.

Cobalt Metal

Carbonylation of Co metal powder was investigated to determine the optimum temperature, pressure, and promoter conditions for use in extracting this metal from the matte, slag, superalloy scrap, and grinding waste. Optimum temperature

TABLE 11. - Metal extraction from superalloy scrap and grinding waste by carbonylation

(2.5- to 10-g charge, 24-h carbonylation, 1,500-psig CO pressure, 0.15-SLM CO flow, 140° C, 20:1 contained (Fe+Ni+Co+Cr)-H_2S promoter mol ratio, and He purge)

	Reduction			Carbonylation					Metal extraction, pct			
	Temp, °C	Reducing gas	Weight loss, pct	Weight loss, pct	Analysis, wt pct Fe	Ni	Co	Cr	Fe	Ni	Co	Cr
Superalloy:												
Ni-base 1	NR	NAp.....	NAp	7.76	0.23	54.2	9.20	18.0	-24.8	11.0	-4.5	-8.7
	710	H_2.....	0.65	[1].89	ND	ND	ND	ND	ND	ND	ND	ND
	710	H_2.....	.65	5.19±0.88	.22±0.01	54.2 ±0.9	8.80±0.42	15.7 ±0.6	-39.1	10.6	2.9	.8
	710	H_2+H_2O..	-7.81	20.21± .59	.40± .05	39.2 ±4.3	7.86±1.32	17.1 ±3.4	-128	34.6	5.9	-14.6
Ni-base 2	NR	NAp.....	NAp	7.98	.23	48.6	10.5	7.77	11.8	26.9	3.4	10.6
	710	H_2.....	-.12	[1]1.06	ND	ND	ND	ND	ND	ND	ND	ND
	710	H_2.....	-.12	4.26	.29	57.2	10.3	7.84	7.4	5.1	.2	3.9
	710	H_2+H_2O..	-3.61	13.60± .35	.32± .06	46.5 ±7.2	9.66±1.75	8.22±1.67	-45.5	22.4	-.2	-6.2
	NR	NAp.....	NAp	3.77	.53	10.2	53.2	22.7	49.0	1.8	7.8	-1.6
Co-base..	NR	NAp.....	NAp	[2]5.33	.32	10.7	57.1	21.1	69.7	-1.4	2.6	7.1
	NR	NAp.....	NAp	[3]9.92	.33	9.70	52.2	21.3	70.3	12.6	15.3	10.8
	710	H_2.....	.24	[1]1.60	ND	ND	ND	ND	ND	ND	ND	ND
	710	H_2.....	.24	[4]2.23	ND	ND	ND	ND	ND	ND	ND	ND
	710	H_2.....	.24	1.98	.47	10.4	55.5	20.9	-9.1	0	0	1.0
	620	H_2+H_2O..	-2.59	.11	.41	10.4	54.3	19.9	0	-2.8	1.1	1.2
	710	H_2+H_2O..	-6.13	.99	.26	8.26	39.3	16.2	33.3	5.5	4.9	5.2
Mixed....	NR	NAp.....	NAp	23.95	11.9	35.2	1.61	14.9	52.4	50.4	-145	12.8
	710	H_2.....	-.04	[1]1.78	ND	ND	ND	ND	ND	ND	ND	ND
	710	H_2.....	-.04	24.67	13.5	41.9	1.03	16.5	41.9	44.1	-81.8	9.3
	710	H_2.....	-.04	[5]31.60	8.46	23.2	1.34	13.0	66.9	71.9	-130	35.8
	710	H_2+H_2O..	-5.52	36.66	9.36	27.4	1.89	16.0	55.1	59.2	-131	3.4
Grinding waste.	NR	NAP.....	NAp	.45	ND	ND	ND	ND	ND	ND	ND	ND
	740	H_2.....	.18	19.59	9.94	11.1	18.0	22.6	71.7	20.4	1.7	7.4
	730	H_2+H_2O..	-4.61	[6]15.40	14.9	9.17	14.7	21.8	57.1	29.0	21.7	15.7

NAp Not applicable. ND Not determined. NR Not reduced.

[1]No H_2S promoter.

[2]Carbonylated at 110° C.

[3]Carbonylated under 1,900 psig CO at 110° C.

[4]80:1 contained (Fe+Ni+Co+Cr)-H_2S promoter mol ratio.

[5]10:1 contained (Fe+Ni+Co+Cr)-H_2S promoter mol ratio.

[6]6.6:1 contained (Fe+Ni+Co+Cr)-H_2S promoter mol ratio.

range for Co-to-$Co_2(CO)_8$ conversion was 110° to 115° C after H_2S activation in a 20:1 Co-H_2S mol ratio. Under these temperatures and promoter conditions, 55 to 60 pct of the Co metal was consistently converted to $Co_2(CO)_8$ in 24 h under 1,500 psig CO. Carbonylation under CO pressure in excess of 1,500 psig did not increase Co conversions. While the optimum temperature range for conversion of pure Co powder to $Co_2(CO)_8$ was 110° to 115° C, this was not the optimum temperature range for conversion of Co to $Co_2(CO)_8$ in matte, slag, scrap, and waste. In most of the latter materials, Co content is low compared with Fe, or it is alloyed with Fe, Ni, or Cr, whose carbonyl conversion parameters control the overall carbonyl formation.

Iron, Steel, and Cast Iron

Carbonylation tests were performed on Fe, steel, cast iron, and other Fe products to answer questions that arose during the course of the research about the reactivity of Fe with CO. Some of the questions were: How does rust or exposure to atmosphere affect conversion to carbonyl; what is the influence of C and other alloying elements in steels and cast irons on carbonyl formation; and how does H_2S promoter influence $Fe(CO)_5$ formation?

The tests showed that visible rust on Fe filings does inhibit carbonyl formation. The Fe filings listed in table 12 responded better to carbonylation after solid-state reduction, which removed the rust color and resulted in a 4.70-pct weight loss. The influence of C and other alloying elements is unclear, although pure Fe and low-carbon steel (AISI-1020) tend to form carbonyls more readily at specific H_2S promoter levels. H_2S promotes the carbonyl reaction, but no definitive Fe-H_2S promoter ratio for optimum carbonyl conversion can be de-

TABLE 12. - Iron, steel, and cast iron conversion to $Fe(CO)_5$

(1- to 10-g charge, 1,500-psig CO pressure, 0.15-SLM CO flow, 140° C, and He purge)

Material	Fe-H_2S mol ratio	Time, h	Weight loss, pct
Reduced Fe filings[1]	None	2	0.26
	92.8:1	2	10.12±0.20
	23.2:1	2	19.94±1.63
	92.8:1	24	23.92
	23.2:1	24	31.00
	[2]18.6:1	6	10.57
AISI-1020 steel filings	92.8:1	2	33.06
	92.8:1	24	61.34
AISI-1045 steel filings	92.8:1	2	19.87±4.48
	92.8:1	24	51.01
AISI-1095 steel filings	92.8:1	2	19.50
	92.8:1	24	40.28
Pig Fe, 4.25 pct C	92.8:1	2	21.32
	92.8:1	24	55.93
Electrolytic Fe powder	92.8:1	2	34.37
	23.2:1	2	55.56
	18.6:1	6	83.03
	46.4:1	24	85.99
Reduced taconite pellets[3]	[4]18.4:1	4	[5]68.21

[1]Reduced at 1,150° C for 22 h with H_2; 4.80-pct weight loss.
[2]Fe filings not reduced.
[3]Reduced at 1,200° C for 16 h with H_2; 28.00-pct weight loss.
[4]Carbonylated at 120° C under 1,200 psig CO.
[5]Estimated 81.2 pct Fe extraction.

fined from the test data. The results are in agreement with previously determined trends involving the use of H_2S promoter. Very limited carbonylation tests on reduced taconite pellets also indicated that carbonyl processing could be a viable approach to extracting the Fe without undue regard for the normal silica and other impurities.

Chromium and Other Metals

A series of carbonylation tests was performed on Cr powder to determine the optimum conditions for producing $Cr(CO)_6$ from the pure metal. The observance of a minute accumulation of $Cr(CO)_6$ in the high-pressure tubing leading from the reactor to the pressure-reduction valve that controlled the flow of CO through the system during chromite Fe extraction studies (34-36) prompted this study. The presence of $Cr(CO)_6$, identified by quantitative chemical analysis, was unexpected because literature reports (38) indicated that $Cr(CO)_6$ is formed by the reaction of suspended $CrCl_3$ in organic solvents with CO in the presence of metallic or inorganic promoters. The only possible sources of Cr were the 410 SS reactor and Cr contained in materials undergoing carbonylation.

No experimental confirmation of $Cr(CO)_6$ formation from the metal was found. Carbonylation tests were performed on minus 100-mesh Cr powder over processing parameter ranges that had resulted in Fe, Ni, and Co carbonyl formation from pure metals, from alloys, and from mineral concentrates. Test conditions ranged as follows: CO pressure from 1,200 to 1,800 psig, temperature from 115° to 205° C, promoter from none to 2.5:1 Cr-H_2S mol ratio, and carbonylation time from 6 to 72 h. Precarbonylation treatment of the Cr powder involved reduction with H_2 and reduction with H_2O-entrained H_2. Two additional carbonylation tests on $CrCl_3$ powder with and without H_2S promoter were also negative. The minute quantities of $Cr(CO)_6$ that were observed may have coformed with $Fe(CO)_5$ during carbonylation, and because of lower volatility, the $Cr(CO)_6$ condensed and concentrated in the cooler tubing.

Other metals and materials subjected to limited carbonylation tests were W, W_3C, WO_3, Mo, Mn, MnO, and Pt. Most of these tests were made under CO pressure, temperature, and H_2S promoter levels found optimum for Fe, Ni, and Co carbonyl formation. No indication of the respective metal carbonyl formation was found in any of these tests.

CONCLUSIONS

Laboratory tests have demonstrated that carbonyl processing can be used to upgrade minerals by removing an undesirable component and to extract the metals Fe, Ni, and Co from minerals, mineral processing byproducts, scrap, and waste. Iron-containing Mn ores are readily upgraded by reducing their Fe oxide fractions to Fe metal and converting the Fe to the volatile $Fe(CO)_5$. Based on this and research reported previously (32-35), carbonyl technology can be utilized to upgrade minerals that contain Fe, Ni, or Co after precarbonylation oxidation and/or reduction treatment when intermetallic alloying is prevented. Iron, nickel, and cobalt can also be extracted from a variety of mineral processing byproducts and wastes by metallization of the respective metal sulfides and oxides prior to carbonylation. The uniqueness of each system mandates that certain details such as the required precarbonylation treatment, particle size, and carbonylation time be determined on an individual basis. The research results indicate that in general, optimum carbonylation was achieved between 110° and 140° C under 100 atm or higher CO pressure and an approximate 20:1 contained metal-H_2S promoter mol ratio. Iron-, nickel-, and cobalt-containing alloys were less responsive to carbonyl processing than materials where the metals are in an elemental-reduced state. Conversion of Cr to the carbonyl was also not consistently achieved in the various materials investigated.

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